RETENTION CAPACITIES OF IMMISCIBLE CHEMICALS IN UNSATURATED SOILS

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Abstract. Retention capacities were measured in the laboratory for n-hexane and tetrachloroethylene (PCE) in three soils at varying soil water contents. Two experimental techniques were used; 1) saturation/drainage experiments where the soil columns were saturated with the chemical and allowed to drain freely for 24 h, and 2) spill simulations where a known amount of chemical was spilled on the surface of the soil column and allowed to infiltrate for one hour. Results show that the retention capacities on a volume basis were independent of chemical type. However, the retention capacities did decrease with decreasing porosity and increasing soil water content. The decrease of retention capacity with respect to soil water content was significant, with the decreases ranging from 38% to 94%. The implication of this decrease is rapid chemical penetration into the subsurface. Retention capacities obtained from spill simulations were consistently lower than those obtained by the saturation/drainage experiments due to hysteresis.

Key words: n-hexane, tetrachloroethylene, unsaturated soil, retention capacity, soil water content

1. Introduction

Organic chemicals are frequently being released into the environment through spills, improper waste disposal and leaking underground storage tanks. Once these chemicals are released into the environment, they can pose an immediate threat to soil, air and groundwater quality. Volatilization of the spilled chemical may pose a health risk in the spill area if the vapours are toxic and may also lead to a potential fire hazard if the vapours are flammable. Infiltration of the chemical results in contaminated soil, while a large enough spill may eventually migrate to the groundwater and pollute drinking water supplies. The chemical retained by the soil presents a long term threat to both air and groundwater quality through volatilization into soil air or dissolution into infiltrating water.

Many factors influence the environmental impact of a chemical release, including the spill volume, chemical and soil properties and the prevailing environmental conditions. Many spilled chemicals have low aqueous solubilities and exist as non-aqueous phase liquids (NAPLs) in soil. The important chemical properties include density, viscosity, vapour pressure, aqueous solubility, surface and interfacial tensions. Soil properties such as particle size distribution, pore size distribution, porosity, hydraulic conductivity, soil chemical composition, soil water content and organic matter content are important. Prevailing environmental conditions such as temperature, wind conditions, rain and/or snowmelt events may have an effect. Mercer and Cohen (1990) provide an excellent review on the above factors and the fate they have on a chemical once it is released into the environment.

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This paper focuses on the retention capacity of unsaturated soils for immiscible chemicals, as it is an important parameter in determining the initial propagation of a spill and in determining whether the contaminant will reach the groundwater (Kia, 1988; Hoag and Marley, 1986). For a given soil and chemical, the retention capacity is generally defined as the amount of chemical the unsaturated soil can hold under the influence of gravity. This includes the chemical trapped in the pores and that sorbed by the soil. In the case of water, the equivalent term is the soil's field capacity. Thus, after a spill, once the retention capacity of a soil is exceeded, the chemical will begin to migrate down through the soil profile. Until that point, chemical movement is limited to either the vapour phase or dissolved phase.

The objective of this research was to experimentally determine, using laboratory prepared soil columns, the retention capacities of three soils at various soil water contents for a lighter-than-water NAPL (LNAPL) and a denser-than-water NAPL (DNAPL). n-Hexane was chosen to represent the group of LNAPLs, with a common LNAPL being gasoline. Tetrachloroethylene (PCE) was chosen to represent the group of chlorinated solvents that are common groundwater contaminants (Anderson *et al.*, 1992). The three soils studied consisted of one purchased soil, Ottawa sand, and two field soils, a loamy sand and a silt loam.

2. Background

The retention capacity is often reported on a volume basis and has units of litres of chemical per cubic meter of porous medium (Schwille, 1984). When expressed as the percent of the pore volume occupied by the chemical, retention capacity is sometimes referred to as the residual saturation, S_r (Anderson *et al.*, 1992; Mercer and Cohen, 1990; Schwille, 1984). The residual saturation can be related to the retention capacity using the following equation:

$$R = S_r \times \phi \times 1000 \tag{1}$$

where ϕ is the porosity.

Previous experimental work has been carried out to determine the retention capacities for different chemicals in soil. However, the majority of the experimental work has involved dry soils, in particular sandy soils low in organic matter content.

Some research groups such as Fine and Yaron (1993), Hoag and Marley (1986), Aurelius and Brown (1987) and McKee *et al.* (1972), have investigated soil water contents other than dry. In general, it was found that retention capacities decreased significantly with increasing soil water content.

In studying different soil types, it was generally observed that retention capacities increased with increasing fines (Hoag and Marley, 1986; Schwille, 1988; Galin *et al.*, 1990). Zytner *et al.* (1993) found particularly high retention capacities of 850 L/m^3 for PCE and 760 L/m^3 for gasoline in peat moss.

3. Materials and Methods

For this study, the retention capacities were measured using two techniques. The first technique, referred to as saturation/drainage experiments, involved saturating a soil column with the chemical and then allowing it to drain freely. The second technique, referred to as spill simulations, involved spilling a fixed volume of chemical on the surface of the soil and allowing it to freely infiltrate and drain through the soil.

Both techniques were carried out using acrylic columns packed with soil. Chemical type, soil type and soil water content were varied in a number of experiments. The following sections outline the materials and procedures used.

3.1. SOILS

Three types of soil were used for the experiments: Ottawa Sand (OS), Delhi Loamy Sand (DLS) and Elora Silt Loam (ESL). These soils were chosen based on their textural class, providing a variety of sand, silt and clay fractions. To ensure consistency of the soil used for different experiments, both the ESL and the DLS were sieved through a 2.0 mm sieve and well-mixed before use. Sieving and mixing was not required for the Ottawa Sand. Table I summarizes the properties of the three soils.

3.2. CHEMICALS

The two chemicals studied were n-hexane (herein referred to as hexane) and tetrachloroethylene, also referred to as perchloroethylene (PCE). Both chemicals were purchased from Fisher Scientific. The chemical grades used were Optima^{TM} grade for hexane and Reagent grade for PCE. Table II summarizes the properties of both chemicals.

3.3. SOIL COLUMNS

Three soil columns made of cast acrylic tubing were used for the saturation/drainage experiments. A typical acrylic column used for the saturation/drainage experiments is illustrated in Figure 1. The column consisted of an outside collar (63.5 mm I.D., 73.0 mm O.D., and 250 mm high) and eleven segments for ease of sampling. All segments had the same inner and outer diameters (49.3 mm I.D., 63.0 mm O.D.) but the heights differed: ten 20 mm high segments and one 50 mm high segment.

The columns were assembled by placing the segments inside the collar, with each segment separated by a Teflon^{TM} gasket. The columns were then closed at each end with lids. There were three different types of lids: a bottom lid, bevelled on the inside to allow drainage towards a 6.4 mm threaded outlet, one top lid with a 37 mm opening and a second top lid with only a pinhole opening. The top lid with the larger opening was used when packing the column, and was replaced before

TABLE I

Soil properties

Soil type	Ottawa sand	Delhi loamy sand	Elora silt loam
% Sand (by weight)	98.8	86.5	34.0
% Silt (by weight)	1.2	9.0	50.1
% Clay (by weight)	0.0	4.5	15.9
Organic Matter (% weight)	0.0	1.2	2.5
CEC (cmol+/kg)	2.3	8.3	10.2
Saturated hydraulic conductivity (m/s)	3.6×10^{-4}	3.8×10^{-5}	3.6×10^{-6}
Bulk density[a] (kg/m^3)	1700–1800	1500–1600	1300–1400
Porosity[b]	0.32–0.36	0.40–0.43	0.47–0.51
Air dry soil water content[c] (% volume)	0	0.9	3.0
Field capacity[d] (% volume)	17	40	48

[a] Range during experiments; within acceptable norms of field values;

[b] Range during experiments; calculated from bulk densities;

[c] Average at beginning of all experiments; measured using standard gravimetric method;

[d] Average at beginning of all experiments after allowing saturated column to drain.

TABLE II

Properties of Hexane and PCE (@ T = 20 °C)

Property	Hexane	PCE
chemical formula	C_6H_{14}	C_2Cl_4
molecular weight	86.2	165.8
density[a] (g/cm^3)	0.66[a]	1.63[a]
water solubility (mg/L)	9.5[a]	200[b]
vapour pressure (kPa)	16.0[a]	1.9[a]
kinematic viscosity[c] (10^{-6} m^2/s)	0.5	0.5
surface tension (10^{-3} N.m^{-1})	18.4[d]	32.9[d]

[a] Verschueren, 1983;

[b] Schwille, 1988;

[c] Calculated;

[d] Mercer and Cohen, 1990

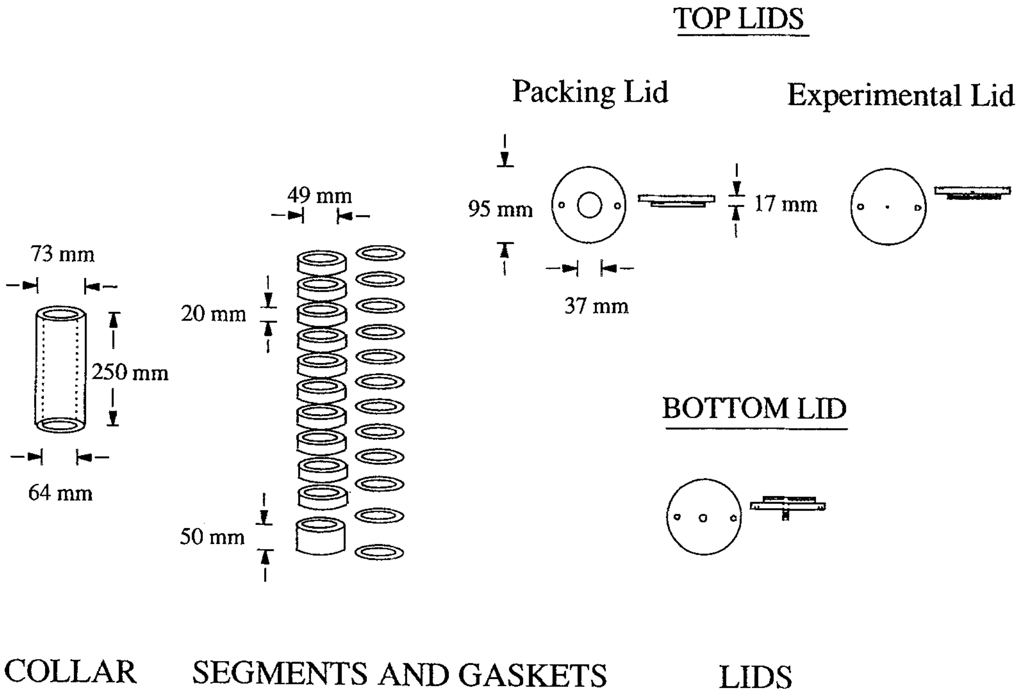

Fig. 1. Column used for retention capacity experiments.

starting an experiment, by the lid with the pinhole opening. The pinhole opening maintained atmospheric conditions while minimizing volatilization losses. The columns were held together using two threaded rods, washers and wing nuts.

The column packing procedure was dependent on the desired soil water content. For air dry (AD) and field capacity (FC), the packing procedure was the same. Gravel and Ottawa Sand were placed at the bottom of the column to provide drainage. Air dry soil was then placed in 50 mm lifts to achieve consistency throughout the column. Each lift was packed to the desired bulk density (Table I) before proceeding to the next lift. For the FC experiment, the prepared columns were then saturated with water and allowed to drain to field capacity for 24 h before using. For the experiments with soils at middle soil water content (MM; a soil water content between AD and FC), the required water was added to the soil before packing.

The spill simulation experiments were conducted in cast acrylic columns similar to the saturation/drainage columns, the only difference being the length of column. The length of the outside collar was increased to 600 mm and contained a total of 19 inside segments: two 100 mm high segments, two 50 mm high segments and fifteen 20 mm high segments. These columns were assembled and packed in the same way as the saturation/drainage columns.

3.4. SATURATION/DRAINAGE EXPERIMENTS

The saturation/drainage experiments were carried out for both chemicals in triplicate, using freshly packed soil columns at the three soil water contents studied; AD, FC and MM. The following steps were carried out for each experiment:

1. All columns were weighed and the mass recorded. One column was placed on an electronic balance equipped for automated data acquisition.
2. The columns were connected as shown in Figure 2 to a common chemical manifold and placed under the fumehood.
3. The soil columns were slowly saturated from the bottom with chemical from the reservoir. Complete saturation was achieved when the chemical ponded at the surface of the soil.
4. Once ponding occurred, valves V_1, V_2 and V_3 (valves leading to the columns) were closed and the reservoir was isolated from the columns by unhooking the chemical feed lines.
5. The column valves V_1, V_2 and V_3 were then reopened and the chemical in the soil was allowed to drain freely. The mass of the column placed on the balance was recorded automatically every minute during drainage.
6. The leachate from the columns was collected only in the experiments involving soils at field capacity or middle soil water content, to determine if water displacement had occurred. If there was evidence of water displacement, the water was separated from the chemical using a separatory funnel and quantified.
7. After 24 hours, the columns were weighed and taken apart. The soil segments were placed in pre-weighed aluminum dishes and weighed. For the experiments at soil water contents other than air dry, the aluminum dishes were covered with Saran Wrap^{TM} to avoid water loss but yet permit volatilization of the studied chemical. This method was also successfully used by Cary *et al.* (1989).
8. Immediately after weighing, the segments were placed under the fumehood to allow passive volatilization of the chemical from the soil. The segments were weighed several times until no further change in mass was observed. The final mass was then recorded. The difference between the final mass and the mass prior to passive volatilization was attributed to chemical loss.
9. Segments at field capacity or middle soil water content were then oven dried at 105°C for 24 hours to determine the actual soil water content.

3.5. SPILL SIMULATIONS

Chemical spill simulations were completed in duplicate for hexane and PCE, in AD Ottawa Sand, AD Elora Silt Loam and in both AD and MM Delhi Loamy Sand. The procedures used are outlined below.

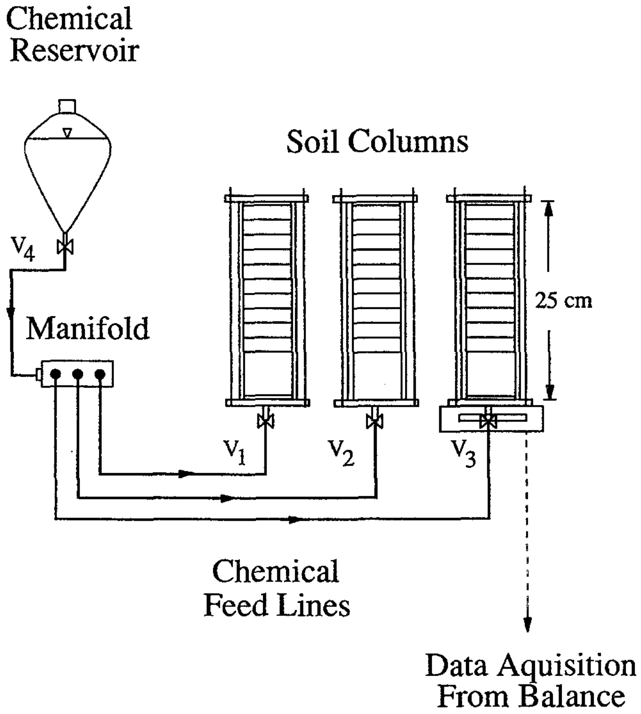

Fig. 2. Experimental apparatus for retention capacity experiments.

3.5.1. *Air dry soils*

1. The packed columns were weighed and the mass recorded.
2. A known amount of chemical was then poured on the surface of the packed soil.
3. As the chemical infiltrated into the soil, both the level of the spilled chemical and the position of the liquid front were recorded.
4. After one hour, at which time no further movement of the wetting front was observed, the column was taken apart. The same procedure as outlined in the saturation/drainage experiments was followed to determine the chemical content of the segments.

3.5.2. *Middle moisture soils*

1. Procedures 1 to 3 as outlined for air dry soils were followed, with the exception that the required amount of water was added to the soil before packing into the column.
2. When chemical breakthrough was observed at the bottom of the column (after approximately one hour), any spilled chemical that remained on the soil surface was removed and the column taken apart. The same procedure as outlined in the saturation/drainage experiments was followed to determine the chemical content of the segments.

4. Results and Discussion

The results obtained in this study have been divided into different sections to facilitate discussion. These include Methods Used to Determine Retention Capacities and Effect of Soil and Chemical Type.

4.1. METHODS USED TO DETERMINE RETENTION CAPACITIES

Two distinct experimental procedures have been used to measure retention capacities: saturation/drainage and spill scenario. The saturation/drainage technique also contains two separate measurements: (1) retention capacity based on the overall mass of the column and (2) retention capacity based on individual segments. In all but 3 cases, the overall mass saturation/drainage experiments had the highest retention capacities. On average, the segments in the saturation/drainage gave a retention capacity at 85% of the absolute value of the overall measure, while the spill scenario values averaged 65% of the absolute value of the overall measure.

The two separate measures based on the saturation/drainage experiments each have their own errors and uncertainties. The retention capacities based on the overall mass measurements are dependent on the correct accounting for chemical retained in the drainage bed below the soil packing. An incorrect accounting of the chemical present will translate into an error, either an over- or underestimation. Since, it appeared in some experiments that the drainage bed did not completely drain, the quantity of chemical in the drainage layer may have been underestimated. This underestimation results in an overestimation of the measured retention capacities. The magnitude of the error will be largest for the lower retention capacities values.

The retention capacities based on the segment measurements are vulnerable to errors due to chemical evaporation during segment handling. Any evaporation of chemical will translate into an underestimation of the retention capacity by this technique. If evaporation was significant, one might suspect a greater discrepancy between the overall and segment measures of retention capacities for the more volatile of the two chemicals, hexane in this case. Since, this was not the case, it suggests evaporation was not significant.

The other uncertainty associated with the segments is the potential for higher retention capacities in the bottom segments, when compared to the segments at the top and middle of the column. Review of all the experimental data indicated that the retention capacity values increased approximately 3–5% from the top to bottom of the column. In OS and DLS experiments, accumulation in the bottom segments was the most pronounced, while with ESL, almost no accumulation was observed in the bottom segments. The accumulation in the lower segments of the column can be attributed to the incomplete drainage that was discussed earlier.

TABLE III

Summary of Hexane and PCE retention capacities (% volume)

Chemical	Soil type	Soil water content	Average retention capacities (% volume)		
			Saturation/drainage experiments		Spill simulations
			overall	segments	segments
Hexane	Ottawa	AD	10.0	7.1	6.4
	Sand	MM	NT	NT	NT
		FC	4.3	4.4	NT
	Delhi	AD	30.0	27.0	17.0
	Loamy	MM	9.3	6.7	9.7
	Sand	FC	4.7	5.4	NT
	Elora	AD	41.0	39.0	28.0
	Silt loam	MM	8.0	5.8	NT
		FC	NP	NP	NT
PCE	Ottawa	AD	9.1	6.0	3.5
	Sand	MM	NT	NT	NT
		FC	4.2	2.9	NT
	Delhi	AD	27.0	27.0	17.0
	Loamy	MM	6.6	4.7	3.9
	Sand	FC	5.6	3.0	NT
	Elora	AD	41.0	39.0	30.0
	Silt Loam	MM	6.9	5.5	NT
		FC	2.5	2.3	NT

NT = Not tested; NP = Not possible.

4.2. RETENTION CAPACITIES

Table III presents a summary of hexane and PCE retention capacities in the three soils at the different soil water contents. The average retention capacities are presented on a volume basis for the entire column. The column values are based on the mass difference of the entire column over the 24 h drainage period, accounting for the chemical present in the drainage layers.

The required 24 h drainage period was determined from the column placed on the mass balance connected to the automated data acquisition system. Review of the data indicated that chemical drainage was complete well within the first 24 hours. In most cases, over 80% of the drainage occurred in the first 2 hours. However, in the case of the spill simulations, retention capacities were measured after only 1 hour, as chemical movement could no longer be visually detected.

Table III also provides retention capacity values based on the average of each of the individual segment retention capacity values. The individual segment values were determined by weighing each segment before and after chemical evaporation.

The influences of chemical type, soil type and soil water content on retention capacities are the same for spill simulations and for saturation/drainage experiments. In general, however, the spill retention capacities are smaller than those obtained during the saturation/drainage experiments. For example, hexane retention capacities in air dry soils vary from 7% to 39% for the saturation/drainage experiments and from an average of 6% to 28% for the spill simulations. For PCE, retention capacities in air dry soils vary from 6% to 41% for saturation/drainage experiments and from 4% to 30% for the spill simulations.

The lower retention capacities in the case of spill simulations versus saturation/drainage experiments may be due to hysteresis, a phenomenon that is well established in soil-water systems. The phenomenon of hysteresis explains the different fluid contents obtained, at a given soil matrix potential, during wetting and drying (or draining) of soils. In general, the soil is wetter during drying than during wetting. This hysteresis is caused by a number of factors, including air entrapment and irregular sizes and shapes of pores (Koorevaar *et al.*, 1983). In the case of the saturation/drainage experiments, the soil column becomes completely saturated, meaning all of the pores are filled, before being allowed to drain. In the spill simulations, the chemical is added to the surface of the soil. With hysteresis, the small pores do not completely fill, due to air entrapment prior to drainage. The volume of these unfilled pores results in a lower retention capacity.

4.3. EFFECT OF SOIL WATER CONTENT

In general, it was observed that the retention capacities decreased as soil water content increased from air dry to field capacity. Hexane retention capacities decrease from 10% to 4% in OS and from 30% to 5% in DLS with the increasing soil water content. The hexane retention capacities in ESL decreased from 41% in the air dry soil to 8% in middle soil water content soil. The hexane retention capacity in field capacity ESL soil could not be determined since hexane was not able to enter the soil column. The same trends were observed for PCE with one exception; PCE was able to enter the soil at field capacity and a retention capacity of 3% was determined. It is believed that PCE's higher fluid density allowed it to overcome any surface tension effects.

The decrease in retention capacity with the increase in soil water content is to be expected. Fine and Yaron (1993), in their study on kerosene residual content (KRC, equivalent of kerosene retention capacity), noticed that an increase in soil water content had a crucial effect on KRC. KRC values decreased by over 30% as soil water content increased. Hoag and Marley (1986) also noticed a decrease in gasoline retention capacities with increasing soil water content.

The variation of retention capacity with soil water content can be explained by considering wettability. Wettability describes the preferential flow of one fluid over solid surfaces in a two-fluid system (Mercer and Cohen, 1990). In the system considered here, the soil is preferentially water-wet: this preferential wetting by water is true of most natural porous media (Mercer and Cohen, 1990). When the chemical is added to the wet soil, it acts as the non-wetting fluid and is therefore limited to accessing the larger pores. Unless the chemical has sufficient pressure to displace the water, the water will remain in the smaller pores and the chemical will only be able to occupy those pores not already occupied by water.

More experiments with additional soil water contents would be useful in further understanding the influence of soil water content on retention capacity. Soil water contents varying from a middle soil water content (13–18% by mass) to field capacity might help explain the difference in hexane and PCE behaviour at higher soil water contents.

4.4. Effect of Soil Type

In air dry soils, the retention capacities of both chemicals vary with soil type. For example, the hexane retention capacities on a volume basis increase from 10% in OS to 30% in DLS and to 41% in ESL based on the overall saturation/drainage values. This same trend is true for the other measures of the retention capacities and for the PCE data. Several factors are likely contributing to the observed behaviour for dry soils. However, the dominant factor is likely the pore size and pore size distribution differences between the three soils. As the silt and clay content increases from OS to DLS to ESL, the pore size decreases, causing an increase in porosity. This results in a subsequent increase in retention capacity. Similar findings were reported by Hausenbuiller (1985) and Anderson *et al.* (1992).

In soils at middle soil water content and field capacity, a strong dependence on soil type was not observed. Retention capacities had a deviation of less than 2% between soil types at these soil water contents. Chemicals retained in moist soils are retained in the medium-sized and larger pores as the water preferentially fills the smallest pores. The distinguishing character between soils of the fraction of the total porosity that results from small pores is lost in the case of the moist soils.

4.5. Effect of Chemical Type

The hexane and PCE retention capacity values reported in Table III show that the retention capacity on a volume basis is relatively independent of chemical type in air dry soils. The PCE values average 85% of the absolute value of the hexane retention capacities. There seems to be somewhat less consistency between the two chemicals for the moist soils. The independence of chemical type is in agreement with the results of Schwille (1981) who found similar retention capacities for oils and chlorinated hydrocarbons.

When comparing the hexane and PCE retention capacities to the field capacities (analogous to the retention capacity of water) in Table I, it can be seen that the field capacities are consistently higher than the retention capacities of both hexane and PCE. The higher field capacities are most likely the result of the higher surface tension of water. The higher surface tension results in a higher capillary pressure and therefore a higher retention capacity. It is believed that the effect of changing surface tension can not be seen between hexane and PCE since the surface tensions are similar. The effect of surface tension can however be seen with water since water has a much greater surface tension than either hexane or PCE.

5. Conclusions

The following conclusions are based on the results of this research:

1. The retention capacities, on a volume basis in dry soils, were independent of immiscible chemical type.
2. Hexane and PCE retention capacities vary with soil type. The retention capacities for both chemicals increase as the silt/clay fraction of the air dry unsaturated soil increases.
3. Increasing soil water contents in unsaturated soil cause a significant decrease in retention capacities, ranging from 38% to 94%.

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